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(54) Title: ADHESIVE COMPOSITIONS CONTAINING LOW MOLECULAR WEIGHT POLYPHENYLENE OXIDES			
(57) Abstract			
<p>Pressure sensitive and hot melt adhesive compositions having improved shear adhesion failure temperatures (SAFT) comprising: (a) a block copolymer having at least two monoalkenyl arene polymer endblocks (A) and at least one elastomeric conjugated-diene midblock (B), said blocks (A) comprising 8-55 % by weight of the block copolymer; (b) about 50 to about 200 phr of a tackifying resin compatible with block (B); and (c) about 5 to about 50 phr of a low molecular weight polyphenylene oxide polymer wherein the molecular weight (<math>M_{vis}</math>) of the polyphenylene oxide polymer is from about 1,000 to about 5,000, the <math>T_g</math> is from about 100° to about 165°C, preferably between 140-163°C.</p>			

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ADHESIVE COMPOSITIONS CONTAINING LOW MOLECULAR WEIGHT  
POLYPHENEYLENE OXIDES

1 This is a continuation-in-part of copending U.S. Serial No.  
2 355,532, filed May 23, 1989, entitled "Adhesive Composition  
3 Containing Low Molecular Weight Polyphenylene Oxides," now  
4 abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The invention relates to the use of low molecular weight  
6 polyphenylene oxides in adhesive blends comprising styrenic triblock  
7 copolymers such as polystyrene-polyisoprene-polystyrene (S-I-S) and  
8 polystyrene-polybutadiene-polystyrene (S-B-S) to provide increases in  
9 the shear adhesion failure temperatures (SAFT) of the corresponding  
10 pressure sensitive, hot melt pressure sensitive or hot melt  
11 adhesives. The SAFT increases are obtained without significant hot  
12 melt formulation viscosity increases and with little impact on the  
13 pressure sensitive adhesives' tack or peel strength.

2. Description of the Prior Art

14 In U.S. Patent 3,660,531, there are disclosed polyblends  
15 containing: (A) greater than 50% of a thermoplastic resin matrix,  
16 said resin matrix consisting of polyphenylene oxide resin in

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1 combination with alkenyl aromatic resins; and (B) less than 50% of an  
2 elastomer selected from a group consisting of poly(butadiene), and  
3 random, block or graft copolymers of butadiene and styrene. The  
4 resulting blends exhibit unexpected thermoplastic properties  
5 including improved melt processability and impact resistance without  
6 sacrificing the desirable heat distortion temperature and flexural  
7 modulus of unmodified polyphenylene oxide resin. The materials in  
8 this patent are thermoplastic resins and not adhesives, and the  
9 degree of polymerization (DP) of polyphenylene oxide is greater than  
10 about 100.

11 Commonly assigned U.S. Patents 3,835,200 and 3,994,856  
12 disclose respectively, polyphenylene ether and rubber styrene  
13 copolymer compositions containing rigid block copolymers of  
14 conjugated dienes and vinyl aromatic compounds, and high impact  
15 rubber modified polystyrene compositions containing polyphenylene  
16 ether and vinyl aromatic block copolymers; however, the compositions  
17 are thermoplastics and the DP of the polyphenylene oxides is greater  
18 than 50.

19 Hot melt adhesive compositions are disclosed in Hansen, U.S.  
20 Patent 4,104,323. The adhesive composition is prepared by first melt  
21 blending a polyphenylene ether resin and a low molecular weight  
22 aromatic resin, and then blending the resulting mixture and a  
23 monoalkenyl arene/conjugated diene block copolymer, tackifying resin,  
24 and optional hydrocarbon processing oil. The molecular weight of the  
25 polyphenylene oxide in the polyphenylene oxide alloy is between 6,000  
26 and 25,000. The glass transition temperature is between 170 and  
27 205°C. This melt blend avoids the use of solvents while also  
28 avoiding oxidative degradation of the block copolymer. The resulting  
29 polymer blend possesses a much higher service temperature when used  
30 as an adhesive.

31 An adhesive composition having improved high temperature  
32 properties is also disclosed in U.S. Patent 4,141,876. The  
33 composition is prepared by melt blending a polyphenylene ether resin,

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1 patent is restricted to hydrogenated block copolymers which can  
2 withstand the extremely high blending temperatures required to  
3 disperse the polyphenylene oxide resins, (230°C to 260°C) and to  
4 polyphenylene oxide resins having a molecular weight ( $M_{vis}$ ) between  
5 6,000 and 25,000. The glass transition temperature of the resin is  
6 restricted to between 170° and 210°C.

## SUMMARY OF THE INVENTION

7 A need exists in the practice of adhesive formulating to  
8 obtain adhesive compositions with higher service temperatures and  
9 manageable hot melt viscosities. The present invention describes the  
10 use of low molecular weight polyphenylene oxide resins (PPO) in hot  
11 melt or pressure sensitive adhesive compositions comprising:

12 (a) 100 phr of a block copolymer having at least two  
13 monoalkenyl arene polymer endblocks A and at least one elastomeric  
14 conjugated-diene midblock B, said blocks A comprising 8-55% by weight  
15 of the block copolymer. Illustrative of the blocks are styrenic  
16 block copolymers such as polystyrene-polybutadiene-polystyrene  
17 (S-B-S), polystyrene-polyisoprene-polystyrene (S-I-S), poly  
18 ( $\alpha$ -methylstyrene)-polyisoprene-poly ( $\alpha$ -methylstyrene), or their  
19 selectively hydrogenated derivatives.

20 (b) about 50-200 phr (part per hundred rubber) of a  
21 tackifying resin compatible with the rubbery midblock of the block  
22 copolymers and

23 (c) about 5-50 phr of a low molecular weight PPO resin with  
24 glass transition temperature ( $T_g$ ) between 100°C and 165°C,  
25 preferably between 140° and 163°C.

26 The tackifying resin, which is compatible with the  
27 elastomeric midblock of the triblock copolymer, is used to render the  
28 formulation tacky. Preferred tackifying resins are those derived  
29 from the copolymerization of diolefins and especially of  $C_5$   
30 diolefins such as piperylene with  $C_5$  olefins such as  
31 2-methyl-2-butene. These resins, such as ESCOREZ 1310LC, available

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1 Lite, available from Arizona Chemicals, is prepared by the cationic  
2 polymerization of limonene and styrene. Other useful tackifying  
3 resins include those derived from rosin esters, terpenes, and terpene  
4 phenolic resins. Hydrogenated versions of the above are also useful.

5 Hydrocarbon extending oils (0-200 phr) can be employed in  
6 this application to modify the formulation viscosity and to increase  
7 the tackiness of the adhesive. The extending oils, referred to as  
8 paraffinic/naphthenic oils are fractions of refined petroleum  
9 products having less than 30% by weight aromatics and viscosities  
10 ranging from 100 to 500 SSU at 100°F. Oils are commercially  
11 available such as Shellflex 371, a naphthenic oil manufactured by  
12 Shell.

13 The adhesive formulations are prepared by dissolving in a  
14 solvent such as toluene, and casting over a substrate such as mylar.  
15 Optionally, to apply the formulation as a hot melt, the components  
16 are melt blended in a Brabender mixer. The temperature for melt  
17 blending will depend upon the  $T_g$  of the PPO. This is a significant  
18 advantage of using PPO of lower  $T_g$  than that claimed in U.S.  
19 Patents 4,104,323 and 4,141,876.

20 The invention discovery is that polyphenylene oxide  
21 copolymers, having low molecular weight and high glass transition  
22 temperatures, extend the temperature range of pressure sensitive and  
23 hot melt adhesive systems which contain styrenic triblock  
24 copolymers. This is a consequence of their compatibilities with the  
25 polystyrene domains of the triblock copolymers used in these adhesive  
26 applications. Because these adhesive formulations are useful up to  
27 the glass transition temperature of the polystyrene domains, blending  
28 a high  $T_g$  PPO polymer into the polystyrene domains increases the  
29  $T_g$  of the glassy domains and consequently increases the useful  
30 temperature range of the adhesive. The glass transition temperature  
31 range for the PPO resin, 100-165°C, preferably 140-163°C enables hot  
32 melt application of the adhesive formulation. Higher  $T_g$  PPO resins  
33 cannot be hot melt processed unless they are preblended with low

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1 invention provide superior adhesive properties compared with the  
2 higher T<sub>g</sub> PPO's.

3         According to the "Glossary of Terms Used in the Pressure  
4 Sensitive Tape Industry", a pressure sensitive adhesive is a material  
5 which is aggressively and permanently tacky, adheres without the need  
6 of more than finger pressure, exerts a strong holding force, and has  
7 sufficient cohesiveness and elasticity that it can be removed from  
8 substrates without leaving a residue. A hot melt adhesive, on the  
9 other hand, is a 100% nonvolatile thermoplastic material that is  
10 heated to a melt and applied to the substrate as a liquid. The hot  
11 melt bond forms after the liquid cools and solidifies. Some pressure  
12 sensitive adhesives, such as those based on block copolymers, are  
13 applied as hot melts, and are referred to as hot melt-pressure  
14 sensitive adhesives.

15         Typically, commercial PPO's are derived from the  
16 2,6-dimethyl phenol monomer. In accordance with this invention there  
17 is described the use of high T<sub>g</sub> PPO copolymers. One advantage of  
18 the use of the copolymers is the lower cost of the monomers such as  
19 o-cresol as compared with the more expensive 2,6-dimethyl phenol  
20 monomer thereby resulting in a lower cost PPO. Further, the use of  
21 comonomers yields the low molecular weight PPO resins which are best  
22 suited for these applications. The useful glass transition  
23 temperature range for these PPO resins ranges from 100-165°C,  
24 preferably between 140-163°C. This range, less than that described  
25 in U.S. Patents 4,104,323 and 4,141,876, provides superior adhesive  
26 service temperature increases while allowing hot melt processibility  
27 below 200°C.

28         These low molecular weight polyphenylene oxides improve the  
29 high temperature performance of styrenic block copolymers in pressure  
30 sensitive adhesive systems. For example, a 7 parts per one hundred  
31 rubber (phr) loading of the PPO in a formulation provides about a  
32 32°F improvement in the shear adhesion failure temperature (SAFT)  
33 with little impact on the pressure sensitive adhesive's tack.

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## DETAILED DESCRIPTION OF THE INVENTION

1           In the use of low molecular weight polyphenylene oxides to  
2   increase the service temperatures of block copolymer adhesive  
3   systems, the upper use temperature of these adhesives is limited to  
4   the softening temperature ( $T_g$ ) of the polystyrene domains. In  
5   accordance with this invention, a high  $T_g$  PPO with good polystyrene  
6   thermodynamic compatibility increases the service temperature when  
7   blended into the adhesive formulation.

8           Block copolymers employed in the invention may have  
9   geometrical structures, however the invention does not depend on a  
10   particular structure, but rather upon the chemical constitution of  
11   each of the polymer blocks. Thus, the structures may be linear,  
12   radial, or branched so long as each copolymer has at least two  
13   polymer endblocks and at least one polymer midblock. Thus the  
14   invention contemplates (but is not limited to) the use of  
15   configurations such as  $(A-B-A)_n$  where  $n$  varies from 1 to 20, and  
16   preferably from 1 to 3, most preferably 1. Methods for preparation  
17   of such polymers are well known in the art. Although the term  
18   triblock is used throughout it is to be understood that where  
19   applicable the radial and branched blocks are included.

20           The invention applies especially to the use of polymers  
21   having the configuration of the following typical species:

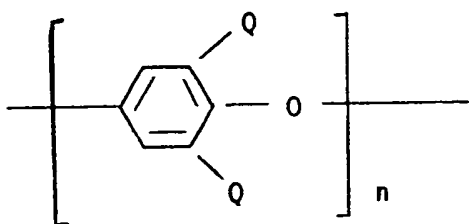
22       polystyrene-polybutadiene-polystyrene (SBS)  
23       polystyrene-polyisoprene-polystyrene (SIS)  
24       poly(alpha-methylstyrene)-polybutadiene-poly  
25       (alpha-methylstyrene) ( $\alpha$ MS-B- $\alpha$ MS)  
26       poly(alpha-methylstyrene)-polyisoprene-poly  
27       (alpha-methylstyrene) ( $\alpha$ MS-I- $\alpha$ MS).

28           It is to be understood that both Blocks A and B may be  
29   either homopolymer or random copolymer blocks as long as each block  
30   predominates in at least one class of the monomers characterizing the  
31   blocks as defined. Thus, blocks A may comprise styrene/alpha-  
32   methylstyrene copolymer blocks or styrene/butadiene random copolymer



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1 analogs and homologs including alpha-methylstyrene and  
 2 ring-substituted styrenes, particularly ring-methylated styrenes.  
 3 The preferred monoalkenyl arenes are styrene and alpha-methylstyrene,  
 4 and styrene is particularly preferred. The blocks B may comprise  
 5 homopolymers of butadiene, isoprene, copolymers of butadiene and  
 6 isoprene and copolymers of one of these two dienes with monoalkenyl  
 7 arene as long as the blocks B predominate in conjugated diene units.  
 8 The rubbery midblock of these polymers may be hydrogenated, but  
 9 non-hydrogenated midblocks can also be used since excessively high  
 10 blending temperatures are not generally required to prepare the  
 11 blends of the present inventory. When the monomer employed is  
 12 butadiene, it is preferred that between about 35 and about 55 mole  
 13 percent of the condensed butadiene units in the butadiene polymer  
 14 block, have a 1,2 configuration.  
 15 Polyphenylene oxides of the invention will have repeating  
 16 units represented by the formula:



17 wherein the oxygen ether atom of one unit is connected to the benzene  
 18 nucleus of the next adjoining unit, n is a positive integer of from  
 19 10 to about 40 thereby providing a MW range of about 1000-5000, and  
 20 each Q is a monovalent substituent selected from the group consisting  
 21 of hydrogen, halogen, hydrocarbon radicals, hydrocarbonoxy radicals,  
 22 and halohydrocarbonoxy radicals having at least two carbon atoms  
 23 between the halogen atom and phenyl nucleus. Especially preferred  
 24 polyphenylene oxide resins for purposes of the present invention are  
 25 those having alkyl substitutions in the two positions ortho to the  
 26 oxygen ether atom - i.e. where each Q is alkyl, most preferably,

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1           The polyphenylene oxides employed in accordance with the  
2 invention, prepared from 2,6-xylenol and additional comonomers such  
3 as o-cresol, allow the cost of the PPO to be materially reduced.  
4 Also, since it is necessary to control the extent of polymerization  
5 to obtain PPO products of low molecular weights, the use of the  
6 comonomers and control of the amount of oxygen admitted to the  
7 reaction allows preparation of the low molecular weights necessary to  
8 the invention.

9           In general, the low molecular weight polyphenylene oxides  
10 are prepared using a cuprous chloride-pyridine catalyst system in  
11 chlorobenzene solution. Magnesium sulfate is used to remove moisture  
12 from the reactions. The products are isolated by precipitation with  
13 a 10% HCl/methanol solution, and are dissolved and reprecipitated to  
14 remove any residual traces of catalyst or diphenoquinone side  
15 products.

16           PPO yields and glass transition temperatures are controlled  
17 by varying the degree of polymerization. This is achieved by  
18 changing the reaction time and consequently the amount of oxygen. A  
19 longer reaction time permits the formation of higher molecular weight  
20 and high  $T_g$  products, which, when precipitated, afford higher  
21 recoveries.

22           Further control of the molecular weight is provided by the  
23 use of o-cresol or other comonomers, which give low degrees of  
24 polymerization with the present catalyst system.

25           Polyphenylene oxides of low molecular weight, useful in the  
26 invention, also can be prepared according to the Perek article in J.  
27 of Polymer Science (vol 25, p 2605) from 4 bromo-2,6-dimethylphenol  
28 as monomer (see Example 5).

#### EXAMPLE 1

29           Cuprous chloride (10g) and pyridine (50ml) are stirred for  
30 30 minutes in 500 ml chlorobenzene. o-Cresol (48ml) and anhydrous  
31 magnesium sulfate (1.5g) are added and the reaction is stirred for 28

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1 solution. The resin is isolated by filtration and washed with  
2 methanol. The yield is 15g (30%) of a pale orange, brittle solid.  
3 The glass transition temperature of the solid is 103°C and H-NMR of  
4 the solid shows a 1:1 ratio of aliphatic to aromatic protons.

## EXAMPLE 2

5 Cuprous chloride (10g) and pyridine (50ml) are stirred for  
6 30 minutes at room temperature in 500 ml chlorobenzene. o-Cresol  
7 (25g), 2,6-xyleneol (25g), and anhydrous magnesium sulfate (1.5g) are  
8 added and the reaction is stirred for 28 hours. The insoluble  
9 portion of the reaction mixture is removed by filtration and the  
10 resin is isolated by precipitation with 10% HCl/methanol. The resin  
11 is isolated by filtration and redissolved in toluene and precipitated  
12 with methanol to remove any residual catalyst or dimeric side  
13 products. The yield is 38g (76%) of a pale orange solid. The glass  
14 transition temperature is 105°C and H-NMR analysis shows a 5:3 ratio  
15 of aliphatic to aromatic protons.

## EXAMPLE 3

16 The procedure of Example 2 is followed except that 26.5g of  
17 2,6-xyleneol and 26.5 g of o-cresol are used. The reaction is stirred  
18 for 48 hours. A 70% yield of a pale orange solid is obtained. The  
19 glass transition temperature of the resin is 153°C and H-NMR analysis  
20 shows a 9:5 ratio of aliphatic to aromatic protons.

## EXAMPLE 4

21 The procedure of Example 1 is followed except that 50g of  
22 2,6-xyleneol is used instead of the o-cresol. Also, the resin is  
23 dissolved in toluene and precipitated with methanol. A 61% yield of  
24 a yellow solid is obtained. The glass transition temperature of the  
25 solid is 154°C and H-NMR analysis of the solid shows a 3:1 ratio of  
26 aliphatic to aromatic protons.

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## EXAMPLE 5

1           4-Bromo-2,6-dimethylphenol (38g) is dissolved in 316 ml 6N  
2 NaOH. Ammonium hydrogen sulfate (5.08g) and 316 ml toluene are  
3 added, and the mixture is stirred for 2 3/4 hours, whereupon, it is  
4 quenched with dilute HCl. The toluene phase is separated and dried  
5 with magnesium sulfate, and the polymer is isolated by precipitation  
6 with methanol (5.5g). DSC and GPC analyses are performed with the  
7 following results:  $T_g=163^{\circ}\text{C}$ ,  $M_n=2600$ ,  $M_w/M_n=1.53$ .

## EXAMPLE 6

8           The procedure of Example 3 was followed except that 75g 2,  
9 6-xylenol, 50 mol pyridine, 900 ml chlorobenzene, and 5g magnesium  
10 sulfate were used. The mixture was stirred for 72 hours. The  
11 polymer yield was 43.5g, and the glass transition temperature was  
12  $145^{\circ}\text{C}$ .

13           In summary, the yields, glass transition temperatures, and  
14 product compositions for the PPO products prepared for testing in  
15 adhesive formulations are as follows:

		<u>GLASS TRANSITION</u>	<u>YIELD</u>	<u>COMPOSITION</u>
		<u>TEMPERATURE</u>		
16	Example 1	103°C	30%	o-Cresol
17	Example 2	105°C	76%	3:4 Xylenol:o-Cresol
18	Example 3	153°C	70%	1:1 Xylenol:o-Cresol
19	Example 4	154°C	61%	Xylenol
20	Example 5	163°C	24%	Xylenol
21	Example 6	145°C	30%	1:1 Xylenol:o-Cresol

22           PPO product compositions were determined using H-NMR  
23 spectroscopy. A ratio of aliphatic protons (1.5-2.5 ppm) to aromatic  
24 protons (6-7.4 ppm) indicates the relative amounts of cresol and  
25 xylenol present in the resins. An entirely 2,6-xylenol product  
26 contains a 3:1 ratio of aliphatic to aromatic protons while an

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1 In the following embodiments, examples and comparisons,  
2 these materials were employed:

- 3 (1) Kraton 1107; a styrene-isoprene-styrene block copolymer from  
4 Shell having block molecular weights of about  
5 13,000-160,000-13,000.
- 6 (2) ESCOREZ 1310LC; a C<sub>5</sub> olefin/diolefin tackifying resin from  
7 Exxon Chemicals having a ring and ball softening point of  
8 95°C.
- 9 (3) Stereon 840A; a tapered styrene-butadiene-styrene block  
10 copolymer from Firestone having Mn of 60,000 and 43 wt %  
11 styrene.
- 12 (4) Zonatac 105L; a limonene/styrene tackifying resin from  
13 Arizona Chemicals having a ring and ball softening point of  
14 105°C.
- 15 (5) Shellflex 371; a naphthenic extending oil from Shell.
- 16 (6) Irganox 1010; an antioxidant from CIBA-Geigy.
- 17 (7) Noryl; a PPO from General Electric having a Tg of 194°C.

#### ADHESIVE TESTING WITH SIS FORMULATIONS

18 S-I-S formulations with E-1310LC as tackifier resin were  
19 prepared for testing as pressure sensitive adhesives. All PPO  
20 products were used at two different levels and the 90° quick stick,  
21 180° peel, polyken tack, and shear adhesion failure temperatures were  
22 measured for each of the formulations. The formulations were cast  
23 from toluene onto mylar, and dried in an oven at 80°C to give a .0015  
24 in. coating.

25 The adhesive tests are those commonly employed by the  
26 pressure sensitive adhesive industry. In the shear adhesion failure  
27 temperature test, a 1"x1" overlap of tape to a stainless steel  
28 substrate is made with a 4.5 pound roller. A 1 kg weight is hung  
29 from the tape and the assembly is placed in an oven. The temperature  
30 is increased at 40°F/hour and the temperature at which the weight

probe contacted the adhesive was recorded.

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1 second dwell time. The force required to break the bond between the  
 2 adhesive and the stainless steel probe is measured (g). The 180°  
 3 peel test involves placing a length of tape on a stainless steel  
 4 plate and laminating it with a 1-pound roller. The force (lb/in)  
 5 required to peel the tape at a 180° angle on an Instron is recorded.  
 6 The results of the adhesive testing are summarized in Table  
 7 1.

TABLE 1

8		<u>1-4</u>	<u>Control</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5-8</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
		<u>Control</u>											
9	KRATON 1107	100	100	100	100	100	100	100	100	100	100	100	100
10	E-1310LC	150	150	150	150	150	150	150	150	150	150	150	150
11	PPO Ex. 1	-	7.3	14.7	-	-	-	-	-	-	-	-	-
12	PPO Ex. 2	-	-	-	7	14	-	-	-	-	-	-	-
13	PPO Ex. 3	-	-	-	-	-	-	7	14	-	-	-	-
14	PPO Ex. 4	-	-	-	-	-	-	-	-	7	14	-	-
15	PPO Ex. 5	-	-	-	-	-	-	-	-	-	-	-	7
16	Irganox 1010	.2	2	2	2	2	2	2	2	2	2	2	2
17	90° Quick												
18	Stick												
19	(lbs/in)	2.3	2.3	2.9	2.6	2.6	1.5	2.7	1.9	1.5	1.1	-	-
20	180° Peel to												
21	SS (lbs/in)	6.4	6.2	6.0	5.9	5.6	4.9	5.1	5.6	4.9	5.3	6.25	6.25
22	Polyken Tack												
23	(g)	1000	702	605	737	350	720	603	495	699	518	1480	1480
24	SAFT												
25	(°F)	200	217	220	229	244	204	234	248	237	244	232	232

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1           It is apparent from Table 1 that the examples representative  
2 of the invention have superior SAFT than those of the comparative  
3 examples. This indicates that lower  $T_g$  PPO resins are also useful  
4 in increasing the service temperatures of adhesives. Finally, the  
5 tack and peel properties of these adhesives are not adversely  
6 affected by the PPO resins as indicated by maintenance of the peel  
7 and quick stick values with modest declines in polyken tack.

8           Figure 1 illustrates the adhesive performance findings for  
9 use of the PPO product of Example 3 with SIS formulations.

#### ADHESIVE TESTING WITH SBS FORMULATIONS

10           Stereon 840 (SBS) formulations with a Zonatac 105 Lite/  
11 Shellflex 371 tackifying system were prepared for testing as hot melt  
12 adhesives. All four PPO products were used at different levels and  
13 the results of the 180° peel and shear adhesion failure temperatures  
14 are compiled in Table 2.

15           Figure 2 illustrates the superior adhesive performance  
16 findings for the use of the PPO product of this invention with SBS  
17 formulations.

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TABLE 2

	<u>1-4 Control</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5-8 Control</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9-12 Control</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
840A	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
105 Lite	120	120	120	120	120	140	134	120	134	120	148	134	120	134	120
•x 371	30	30	30	30	30	28	28	28	28	28	-	-	-	-	-
1	-	5	10	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	5	10	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	14	28	-	-	-	14	28	-	-
4	-	-	-	-	-	-	-	-	14	28	-	-	-	14	28
1010	2	2	2	2	2	2	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
•el to 88 */(in)	4.2	2.5	2.9	2.6	1.5	4.4	3.8	1.8	5.8	0.9	3.2	1.9	1.5	3.0	0.7
SA: (•)	160	176	184	193	213	165	197	214	203	216	170	200	220	216	235



TABLE 3: FORMULATION VISCOSITY PROFILE

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
1 <b>Kraton 1107</b>	<b>4g</b>	<b>4g</b>	-	-
2 <b>Stereon 840A</b>	-	-	<b>3.6g</b>	<b>3.6g</b>
3 <b>Escorez 1310LC</b>	<b>6g</b>	<b>6g</b>	-	-
4 <b>Zonatac 105Lite</b>	-	-	<b>5.4g</b>	<b>4.3g</b>
5 <b>PPO Ex.3</b>	-	<b>0.6g</b>	-	-
6 <b>PPO Ex. 4</b>	-	-	-	<b>1.0g</b>
7 <b>Shellflex 371</b>	-	-	<b>1.0g</b>	<b>1.0g</b>
8 <b>Viscosity (Ps)</b>				
9 <b>180°C</b>	<b>764</b>	<b>710</b>	<b>146</b>	<b>392</b>
10 <b>200°C</b>	<b>280</b>	<b>302</b>	<b>88</b>	<b>173</b>
11 <b>220°C</b>	<b>120</b>	<b>94</b>	<b>57</b>	<b>96</b>

12 The viscosity results indicate that the PPO products of the  
 13 invention can be formulated into adhesive formulations for hot  
 14 melts without significantly altering the viscosity profile.

15         Stereon 840 (SBS) formulations with a Zonatac 105  
 16 Lite/Shellflex 371 tackifying system were prepared for testing as  
 17 hot melt adhesives and solvent cast pressure sensitive adhesives.  
 18 For the purpose of comparison of the PPO's of this invention with  
 19 the PPO's of the prior art, the formulations were prepared with the  
 20 PPO of Example 6 (Tg=145°C) and NORYL (Tg=194°C). For the hot melt  
 21 adhesive, viscosity, T-Peel, SAFT and PAFT were evaluated. For the  
 22 solvent cast pressure sensitive adhesive, 180° peel and SAFT were  
 23 evaluated.

24         The T-Peel test was performed according to the procedure  
 ASTM D1876-70 for both aluminum and polyethylene. The shear

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1 above, except that a 500 g weight was used for a 1" x 1" overlap of  
2 Kraft paper bonded to Kraft paper. The peel adhesion failure  
3 temperature (PAFT) utilized the same geometry as the ASTM D-1876-72  
4 T-Peel test except with a 1" x 1" overlap of Kraft paper bonded to  
5 Kraft paper. The PAFT evaluation was conducted in an oven with a  
6 200 g weight attached. The reported temperature was the  
7 temperature at which the bond failed when the oven was ramped at  
8 40°F/hour. The 180° peel test was as described above. The results  
9 of the adhesive testing are summarized in Table 4.

10 While the invention has focused on the use of certain  
11 particular low molecular weight PPO polymers having a  $T_g$  of about  
12 100°C to about 165°C to improve the upper temperature performances  
13 of styrene block copolymer adhesive systems, it is to be understood  
14 that a wide range of these polymers are suitable and that the  
15 compositions can be dictated by economic considerations. For  
16 example, the data show that cresol copolymers exhibited  
17 performances comparable to the more expensive xylenol homopolymer.  
18 Therefore, many monomer combinations based on cresylic acids and  
19 phenol methylation products can be used without departing from the  
20 spirit and scope of the use of low molecular weight PPO polymers  
21 for high temperature applications in pressure sensitive and hot  
22 melt adhesive systems.

TABLE 4: PPO T<sub>g</sub> COMPARISON

		<u>Hot Melt Adhesive</u>		<u>Solvent Cast PSA (from toluene)</u>	
		<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
1	STEREON 840A	100	100	100	100
2	Zonatac 105 Lite	120	120	120	120
3	Shellflex 371	38.6	38.6	38.6	38.6
4	PPO Ex. 6				
5	(T <sub>g</sub> =145°C)	38.6	--	38.6	--
6	NORYL PPO				
7	(T <sub>g</sub> =194°C)	--	38.6	--	38.6
8	Brookfield Viscosity				
9	180°C	24,450 cps	--*		
10	200°C	11,500 cps	--*		
11	T-Peel (lb/in.)				
12	Al/Al	7.1	--*		
13	PE/PE	0.1	--*		
14	SAFT (°F)				
15	1" x 1" x 500g				
16	Kraft/Kraft	200	--*		
17	PAFT (°F)				
18	1" x 1" x 100g				
19	Kraft/Kraft	212	--*		
20	180°Peel (lb/in.)				
21	SS			2.5	0.2
22	SAFT (°F)				

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1           The most remarkable feature of the data presented in Table 4  
2 is that the NORYL (tg=194°C) could not be hot melt blended at  
3 temperatures up to 220°C, in contrast to the low Tg (145°C) PPO of  
4 example 6. Furthermore, the adhesive properties of the lower Tg PPO  
5 of Example 6 formulations are superior to properties achieved with  
6 the higher Tg NORYL resin formulations. These data demonstrate a  
7 clear advantage in processability and in adhesive performance for the  
8 low Tg PPO compositions of this invention versus the higher Tg PPO  
9 resins taught in the prior art.

CLAIMS:

1. An adhesive composition having improved shear adhesion failure temperatures (SAFT) comprising:

(a) 100 phr of a block copolymer having at least two monoalkenyl arene polymer endblocks A and at least one elastomeric conjugated-diene midblock B, said blocks A comprising 8-55% by weight of the block copolymer;

(b) about 50 to about 200 phr of a tackifying resin compatible with block B; and

(c) about 5 to about 50 phr of a low molecular weight polyphenylene oxide polymer, having a molecular weight ( $M_{vis}$ ) between about 1000 and about 5,000, and a  $T_g$  of about 100°-165°C.

2. The composition of claim 1 wherein the block polymer is a triblock.

3. The composition of claim 1, wherein the polyphenylene oxide polymer has a  $T_g$  of about 140°-163°C.

4. The composition of claim 2, wherein the triblock copolymer comprises styrene endblocks and a polyisoprene rubbery midblock.

5. The composition of claim 2, wherein the triblock copolymer comprises styrene endblocks and a butadiene rubbery midblock.

6. The composition of claim 1, wherein the block copolymer is a triblock copolymer having styrene- $\alpha$ -methylstyrene endblocks and a polyisoprene rubbery midblock.

7. The composition of claim 3, wherein the block copolymer

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8. The composition of claim 3, wherein the block copolymer is a triblock copolymer having styrene endblocks and a butadiene rubbery midblock.

9. The composition of claim 3, wherein the block copolymer is a triblock copolymer having styrene-alpha-methylstyrene endblocks and a polyisoprene rubbery midblock.

10. An adhesive tape comprising the adhesive composition of claim 1.

11. A substrate coated with the adhesive composition of claim 1.

12. The composition of claim 4, wherein the block copolymer is hydrogenated.

13. The composition of claim 7, wherein the block copolymer is hydrogenated.

14. The substrate of claim 12, wherein the substrate is metallic.

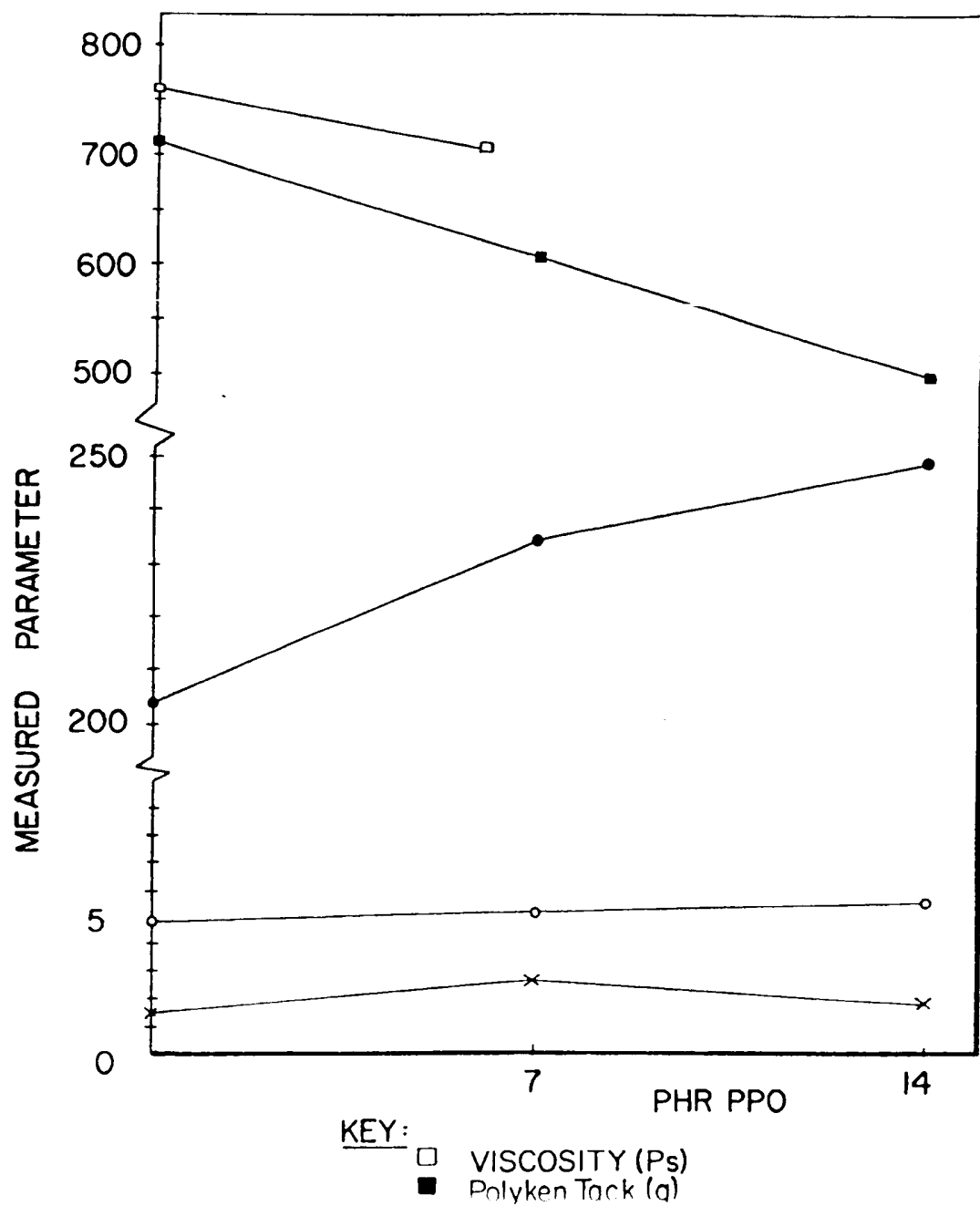
15. A hot melt adhesive comprising the composition of claim 1.

16. A pressure sensitive adhesive comprising the composition of claim 1.

17. A hot melt pressure sensitive adhesive comprising the composition of claim 1.

**Fig. 1**

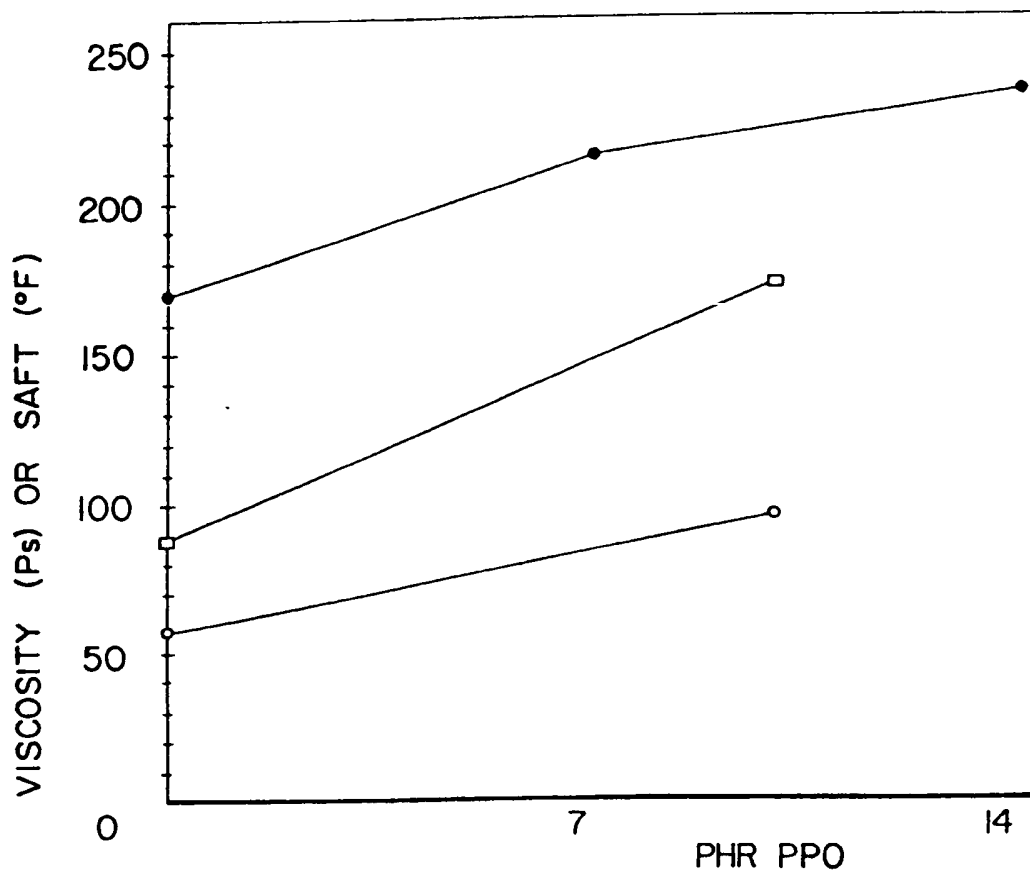
GRAPH 1: SIS/ EXAMPLE 3 PPO



90° Quick Stick (lbs/in)

**Fig. 2**

GRAPH: 2 SBS/EXAMPLE 3 PPO

KEY:

- SAFT (°F)
- Viscosity (Ps) at 200°C
- Viscosity (Ps) at 220°C



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/02948

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 09 J 153/02																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>5</sup></td> <td style="padding: 5px;">C 09 J, C 08 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>5</sup>	C 09 J, C 08 L											
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IPC <sup>5</sup>	C 09 J, C 08 L																
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>10</sup></th> <th style="border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 10%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">EP, A, 0001306 (SHELL) 4 April 1979 see claims (cited in the application)</td> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">--</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">DE, A, 2222230 (ASAHI DOW) 15 November 1973 see claims</td> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">-----</td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	EP, A, 0001306 (SHELL) 4 April 1979 see claims (cited in the application)	1-17	--			Y	DE, A, 2222230 (ASAHI DOW) 15 November 1973 see claims	1-17	-----		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>14</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"G" document member of the same patent family</p> </div> </div>																	
<b>IV. CERTIFICATION</b> <div style="display: flex; justify-content: space-between; font-size: small;"> <div>Date of the Actual Completion of the International Search</div> <div>Date of the International Search Report</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 45%;"> <p style="text-align: center;">INTERNATIONAL SEARCHING AUTHORITY</p> <p style="text-align: center;">EUROPEAN PATENT OFFICE</p> </div> <div style="width: 45%; text-align: right;"> <p>Signature of Authorized Officer</p> <p><i>Natalie Weinberg</i></p> </div> </div>																	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9002948  
SA 37881

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0001306	04-04-79	US-A- 4141876	27-02-79
		AT-B- 362480	25-05-81
		AU-B- 517163	09-07-81
		AU-A- 4005478	27-03-80
		CA-A- 1133159	05-10-82
		JP-A, B, C54056636	07-05-79
DE-A- 2222230	15-11-73	FR-A, B 2182695	14-12-73
		GB-A- 1393728	14-05-75
		NL-A- 7206025	06-11-73